Stereoselective Allylation and Reduction of *N-tert*-Butanesulfinyl-α-keto Aldimines

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Dedicated to the memory of Professor Howard Flack

Abstract- A simple methodology for the synthesis of *N-tert*-butanesulfinyl-α-keto aldimines from both α-keto aldehydes and carboxylic esters has been developed. The addition of an in situ formed allyl indium reagent to these chiral imines was also studied. The addition took place in a sequential manner, first to the imine group with excellent diastereoselectivity and then, to the carbonyl group in a lower diastereoselective fashion. Ruthenium-catalyzed ring closing metathesis of the resulting 5-aminoocta-1,7-dien-4-ol derivatives provided access to 6-aminocyclohex-3-enols. Reduction of the α-keto aldimines led to *N-tert*-butanesulfinyl-1,2-aminoalcohols as a 1:1 diastereomeric mixture.

1. Introduction

The amine functionality is widely present in drugs and drug candidates.[1] Actually, more than 75% of these compounds are aminated derivatives. This functionality is also abundant in natural products, many of them displaying interesting biological activities, catalysts and materials.[2] Due to the fact that in most of these compounds the nitrogen atom is bonded to a stereogenic center, especially in naturally occurring products, the development of new synthetic methodologies for their preparation in an efficient, reliable and simple manner, is of great interest. The most useful procedures involve the reduction of ketimines or the nucleophilic addition of organometallic compounds to aldimines.[3] The presence of a electron withdrawing group on the nitrogen of the imine facilitates the nucleophilic addition and in many cases it behaves as a protecting group of the resulting amine derivative. At this point, it is worth mentioning that *N-tert*-butanesulfinyl imines have found high applicability in synthesis,[4] because they can be prepared in large-scale processes from the corresponding carbonyl compound and commercially available in enantiomerically pure form at reasonable prices *tert*-butanesulfinamide.[5] The *tert*-butanesulfinyl group can be removed easily under acidic conditions from these compounds to give free amines and, in addition, useful synthetic procedures have been developed in order to recycle the chiral *tert*-butanesulfinamide.[6] Regarding our previous work in this area, we have described the stereoselective indium promoted coupling of *N-tert*-butanesulfinyl imines with allylic bromides[7] and alcohols,[8] also with trimethylsilyl propargyl bromide.[9] The resulting homoallyl and homopropargyl amine derivatives, respectively, were used as precursors in the synthesis of natural products[10] and other structurally diverse nitrogen-containing compounds.[11] More recently, the indium-mediated diastereoselective allylation of *N-tert*-butanesulfinyl imines derived from α-ketoesters were also studied.[12] Continuing our interest in this topic, we report herein our first approach to the indium-mediated allylation and also the reduction of *N-tert*-butanesulfinyl imines derived from α-ketoaldimines. The nucleophilic addition to these compounds with two potential electrophilic positions has not been studied yet.

Keywords: α-keto imines, sulfinyl imines, diastereoselective allylation, 1,7-octadienes, aminocyclohexenols, 1,2-aminoalcohols
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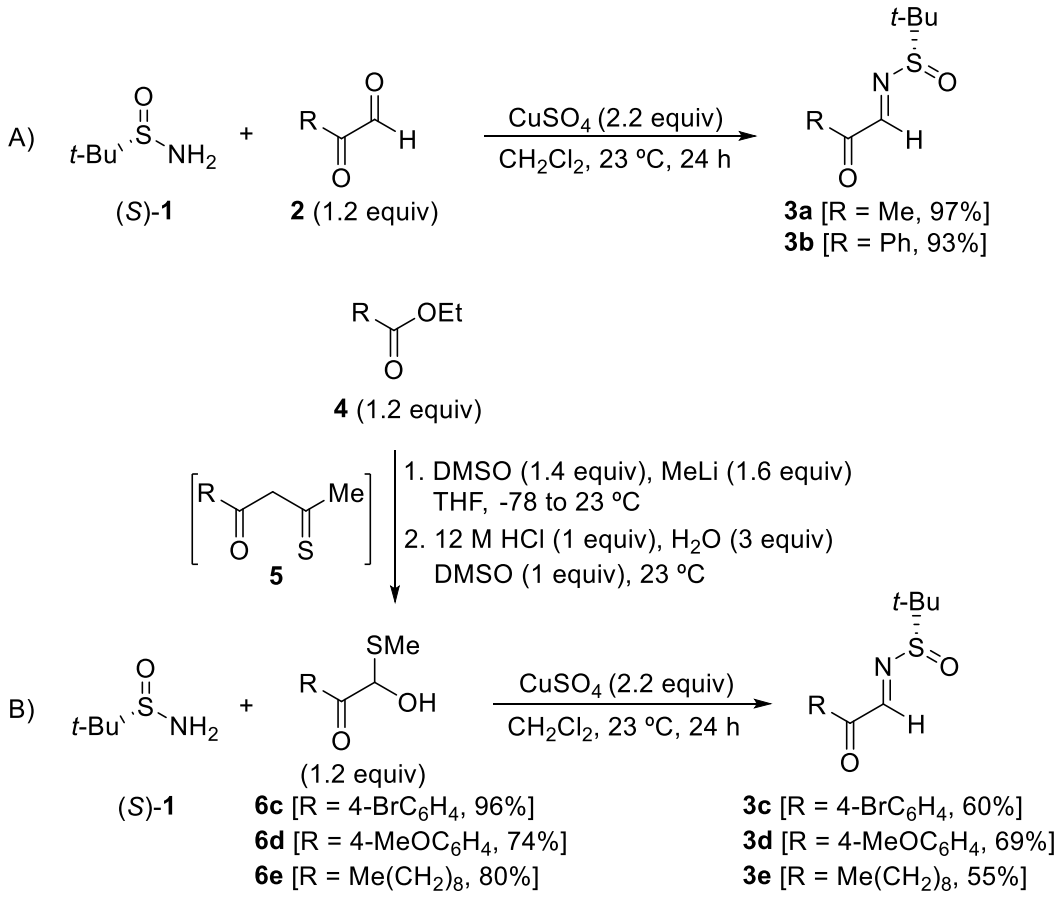
2. Results and discussion

Starting α-keto aldimines **3a** and **3b** were prepared in high yields by direct condensation of commercially available methylglyoxal (**2a**) and phenylglyoxal (**2b**), respectively, with (*S*)-*tert*-butanesulfinamide (**1**), in the presence of $CuSO_4$ in dichloromethane at room temperature (Scheme 1A).[13] The same reaction conditions worked also for the direct condensation of α-ketohemithioketals **6c**-**e** and (*S*)-*tert*-butanesulfinamide (**1**) to produce α-keto aldimines **3c**-**e**, although in moderate yields. These α-ketohemithioketals **6c**-**e** behave as α-keto aldehyde surrogates and were prepared from the corresponding ethyl esters **4** by reaction with dimsyl anion to give β-keto sulfoxide intermediates **5**,[14] which under controlled acidic conditions led to compounds **6c**-**e** (Scheme 1B).[15]

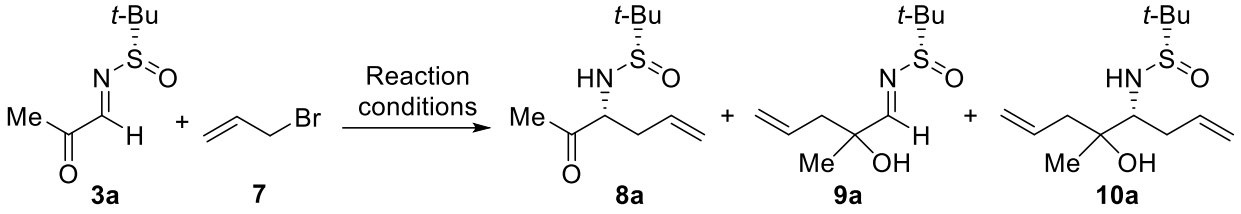


Scheme 1. Synthesis of *N*-*tert*-butanesulfinyl-α-keto aldimines **3**

We decided to study the indium-mediated allylation of these α-keto aldimines **3** with allyl bromide (**7**), paying attention to the chemo- and stereoselectivity of the process. For that reason, we took the chiral imine **3a** derived from methylglyoxal (**2a**) as model compound for the optimization of the reaction conditions. Thus, the reaction of imine **3a** with 1.0 equiv of allyl bromide (**7**) and 1.5 equiv of indium metal in THF at 5 °C for 14 h led to a mixture of monoallylated product **9a**, along with a significant amount of starting material **3a** (Table 1, entry 1). When the reaction was performed at the same temperature but, using 3.0 equiv of allyl bromide (**7**) and 2.5 equiv of indium, and 1:1 mixture of starting imine **3a** and homoallylalcohol **9a** was obtained (Table 1, entry 2). Surprisingly, when the allylation reactions were performed at room temperature in the presence of 1.0 and 3.0 equiv of allyl bromide (**7**) the results were quite different. With 1.0 equiv of **7**, the homoallylamine derivative **8a** was now the major component of the reaction mixture (Table 1, entry 3). The allylation at room temperature with excess (3.0 equiv) of allyl bromide (**7**) produced exclusively compound **10a**, resulting from a double allylation (Table 1, entry 4). Similar results to those

obtained working at room temperature were found at 60 °C (Table 1, entries 5 and 6). We observed that the addition to the imine took place in an almost total diastereoselective manner (*Re*-face addition to imines with S_S configuration). However, subsequent addition to the carbonyl was less diastereoselective, leading to mixture of diastereoisomers in a 2:1 to 3:1 ratio.

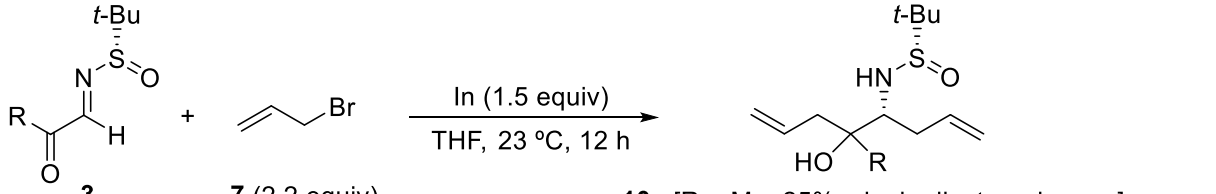
Table 1. Optimization of the allylation reaction conditions[a]



Entry	Reaction conditions	Ratio[b]			
		3a	**8a**	**9a**[c]	**10a**
1	**7** (1 equiv), In (1.5 equiv), THF (2 mL), 5 ºC, 14 h	85	0	15	0
2	**7** (3 equiv), In (2.5 equiv), THF (2 mL), 5 ºC, 14 h	50	0	50	0
3	**7** (1 equiv), In (1.5 equiv), THF (2 mL), 23 ºC, 6 h	10	65	25	0
4	**7** (3 equiv), In (2.5 equiv), THF (2 mL), 23 ºC, 6 h	0	0	0	100
5	**7** (1 equiv), In (1.5 equiv), THF (2 mL), 60 ºC, 6 h	0	64	30	6
6	**7** (3 equiv), In (2.5 equiv), THF (2 mL), 60 ºC, 6 h	0	0	0	100

[a] Reactions were carried out with 0.5 mmol of **3a**. [b] Ratio was determined from the ^{1}H NMR spectrum of the crude reaction mixture. [c] Formed as a 2:1 to 3:1 mixture of diastereoisomers.

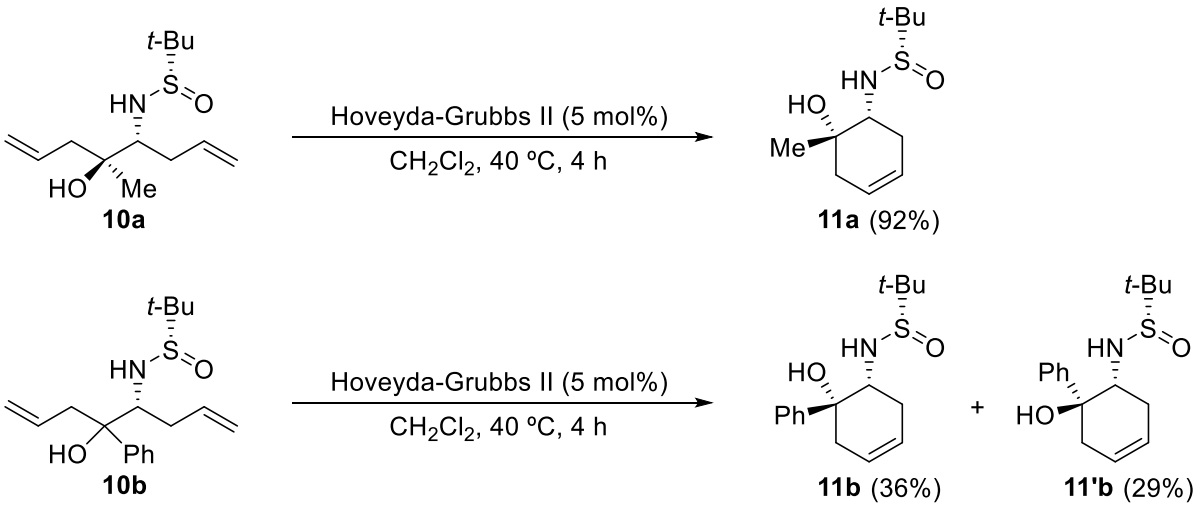
We studied next the reaction of different *N*-*tert*-butanesulfinyl-α-keto aldimines **3** with allyl bromide (**7**), by applying the optimized conditions shown in Table 1, entry 4, in order to produce the reaction products **10** resulting from the double allylation. Interestingly, compounds **10** were obtained in moderate yields with high diastereoselectivity for aliphatic derivatives {**10a** (R = Me) and **10c** [R = Me$(CH_2)_8$]}, and as a mixture of stereoisomers as a consequence of the lack of diastereoselectivity in the allylation step of the carbonyl group for phenyl substituted compound **10b**. Yields shown of Scheme 2 refer to the isolated products after column chromatography purification,.



10a [R = Me, 25%, single diastereoisomer]
10b [R = Ph, 40%, 3:2 diastereomeric mixture]
10e [R = Me$(CH_2)_8$, 37%, single diastereoisomer]

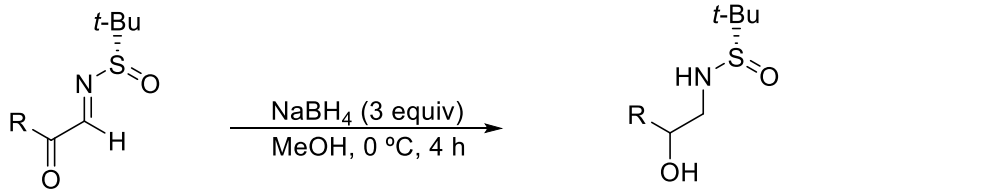
Scheme 2. Double allylation of *N*-*tert*-butanesulfinyl-α-keto aldimines **3**

Double allylated amino alcohol derivatives **10** are interesting building blocks. For instance, ring-closing metathesis (RCM) of these compounds by means a Hoveyda-Grubbs second generation ruthenium catalyst[16] produced *N-tert*-butanesulfinyl-6-aminocyclohex-3-en-1-ol derivatives **11** (Scheme 3). Starting from diene **10a**, compound **11a** was isolated in 92% yield. The relative configuration of **11a** was determined to be *cis* after NOESY experiments, so we assumed that the addition to the carbonyl group in the second allylation step leading to compounds **10** (Scheme 2), took place preferentially to the *Re*-face. The RCM of a 3:2 diastereomeric mixture of **10b** led to aminocyclohexenol derivatives **11b** and **11'b** in a 65% overall yield. These compounds were easily separated after column chromatography and subsequently characterized as single isomers (Scheme 3).



Scheme 3. Synthesis of aminocyclohexenol derivatives **11**

In addition, *N-tert*-butanesulfinyl-1,2-aminoalcohol derivatives **12** were also prepared by reduction of the α-keto aldimines **3** with sodium borohydride in methanol. Unfortunately, an almost 1:1 mixture of diastereoisomers was obtained in all cases which could not be easily separated (Scheme 4). These 1,2-aminoalcohol derivatives could be of potential interest as chiral ligands in different catalytic processes. Further studies regarding the use of more selective reducing agents are in progress at present, along with the chemoselective oxidation of compounds **12** leading to aminomethyl ketone derivatives.



12a [R = Me, 84%, 60:40 dr]
12b [R = Ph, 54%, 59:41 dr]
12c [R = 4-BrC_6H_4, 78%, 56:44 dr]
12d [R = 4-$MeOC_6H_4$, 89%, 57:43 dr]
12e [R = $Me(CH_2)_8$, 56%, 54:46 dr]

Scheme 4. Reduction of *N-tert*-butanesulfinyl-α-keto aldimines **3**

3. Conclusion

In summary, 5-aminoocta-1,7-dien-4-ol derivatives with alkyl or aryl substituents at the 4-position were prepared by double allylation of *N*-*tert*-butanesulfinyl-α-keto aldimines promoted by indium. The allylation of the imine group took place in an almost diastereoselective manner, the addition to the carbonyl group being less stereoselective. This methodology made use of indium metal which is nontoxic and do not require exclusion of moisture and air. Ring closing metathesis of substituted octadienes led to the formation of the corresponding 3-aminocyclohex-2-enol derivatives. In addition, *N*-*tert*-butanesulfinyl-1,2-aminoalcohols were also accessible by reduction of the starting α-keto aldimines, although as a *c.a.* 1:1 mixture of diastereoisomers.

4. Experimental

4.1. General

(S_S)-*tert*-Butanesulfinamide and its enantiomer were a gift of Medalchemy (> 99% ee by chiral HPLC on a Chiracel AS column, 90:10 *n*-hexane/*i*-PrOH, 1.2 mL/min, λ = 222 nm). TLC was performed on silica gel 60 F_{254}, using aluminum plates and visualized with phosphomolybdic acid (PMA) stain. Flash chromatography was carried out on handpacked columns of silica gel 60 (230-400 mesh). Melting points are uncorrected. Optical rotations were measured using a polarimeter with a thermally jacketted 5 cm cell at approximately 20 ºC and concentrations (*c*) are given in g/100 mL. Infrared analyses were performed with a spectrophotometer equipped with an ATR component; wavenumbers are given in cm^{-1}. Low-resolution mass spectra (EI) were obtained at 70 eV; and fragment ions in *m/z* with relative intensities (%) in parentheses. High-resolution mass spectra (HRMS) were also carried out in the electron impact mode (EI) at 70 eV and on an apparatus equipped with a time of flight (TOF) analyzer and the samples were ionized by ESI techniques and introduced through an ultra-high pressure liquid chromatography (UPLC) model. ^{1}H NMR spectra were recorded at 300 or 400 MHz for ^{1}H NMR and 75 or 100 MHz for ^{13}C NMR, using $CDCl_3$ as the solvent and TMS as internal standard (0.00 ppm). The data are being reported as: s = singlet, d = doublet, t = triplet, q = quadruplet, h = septuplet, m = multiplet or unresolved, br s = broad signal, coupling constant(s) in Hz, integration. ^{13}C NMR spectra were recorded with ^{1}H-decoupling at 100 MHz and referenced to $CDCl_3$ at 77.16 ppm. DEPT-135 experiments were performed to assign CH, CH_2 and CH_3.

4.2. General procedure for the synthesis of hemithioketals 6:

To a solution of dimethyl sulfoxide (1.10 g, 1.0 mL, 14.0 mmol) in THF (15 mL) was added dropwise a 1.6 M solution of methyllithium in Et_2O (6.0 mL, 9.6 mmol) at 0 ºC. After 1 h at this temperature, the corresponding ethyl ester **4** (7.0 mmol) was added, and stirring was continued for 12 h at room temperature. To the reaction mixture was successively added water (15 mL) and chloroform (15 mL). Then it was acidified to pH 2-3 with 1 M hydrochloric acid and extracted with chloroform (3×10 mL). The organic layer was dried over anhydrous magnesium sulfate and evaporated (15 Torr). The resulting residue was the corresponding β-ketosulfoxide **5** pure enough to be used in the next step. Thus, to a solution of the corresponding β-ketosulfoxide **5** (7.0 mmol) was successively added water (18 mL) and a 12 M hydrochloric solution (0.5 mL, 6.0 mmol) at room temperature and stirring was mantained for 24 h. When a solid was formed, it was filtered off, washed with cold water and dried under vacuum to give pure products **6c** and **6d**. For the aliphatic derivate, the reaction mixture was extracted with ethyl acetate (3×10 mL). The organic layer was

dried over anhydrous magnesium sulfate and evaporated (15 Torr) to give pure product **6e**. Yields, physical and spectroscopic data for these compounds follow.

4.2.1. 1-(4-Bromophenyl)-2-hydroxy-2-(methylthio)ethan-1-one (6c): The representative procedure was followed by using ethyl ester **4c** (1.60 g, 1.14 mL, 7.0 mmol). Compound **6c** (1.754 g, 6.72 mmol, 96%) was obtained as a orange solid, mp 76-77 ºC (hexane/CH_2Cl_2); R_f 0.11 (hexane/EtOAc, 2:1); IR (neat) ν 2961, 1711, 1480, 1325, 1283, 1193, 1072, 854, 715 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.98 (3H, s, CH_3), 6.08 (1H, s, CH), 7.64 (2H, d, J = 8.7 Hz, 2×CH), 7.91 (2H, d, J = 8.7 Hz, 2×CH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 10.1 (CH_3), 74.7 (CH), 129.6 (C), 130.4 (CH), 131.2 (C), 132.1 (CH), 192.8 (C) ; LRMS (EI) *m/z* 214 (M^+–47, 22%), 212 (25), 184 (95), 182 (100), 156 (35), 154 (40); HRMS calcd for $C_8H_6Br^{79}O_2$ (M^+–CH_3S): 212.9551; found: 212.9560.

4.2.2. 2-Hydroxy-1-(4-methoxyphenyl)-2-(methylthio)ethan-1-one (6d): The representative procedure was followed by using ethyl ester **4d** (1.26 g, 1.13 mL, 7.0 mmol). Compound **6d** (1.01 g, 5.18 mmol, 74%) was obtained as a orange solid, mp 73-74 ºC (hexane/CH_2Cl_2); R_f 0.09 (hexane/EtOAc, 2:1); IR (neat) ν 2940, 1713, 1480, 1330, 1320, 1281, 1160, 850 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.00 (3H, s, CH_3), 3.89 (3H, s, CH_3), 6.08 (1H, s, CH), 6.97 (2H, d, J = 8.7 Hz, 2×CH), 8.05 (2H, d, J = 8.7 Hz, 2×CH); ^{13}C NMR (100 MHz, $CDCl_3$) 11.5 (CH_3), 55.6 (CH_3), 77.2 (CH), 113.8 (CH), 114.3 (CH), 121.4 (C), 132.3 (CH), 133.4 (CH), 164.0 (C), 193.8 (C); LRMS (EI) *m/z* 165 (M^+–47, 24%), 135 (100), 107 (60), 77 (34).

4.2.3. 1-Hydroxy-1-(methylthio)undecan-2-one (6e): The representative procedure was followed by using ethyl ester **4e** (1.40 g, 1.62 mL, 7.0 mmol). Compound **6e** (1.30 g, 5.60 mmol, 80%) was obtained as a yellow oil; R_f 0.21 (hexane/EtOAc, 2:1); IR (neat) ν 2939, 2910, 2805, 1692, 1435, 1375 1201, 1111, 1078, 922 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.85 (3H, t, J = 6.9 Hz, CH_3), 1.22-1.28 (14H, m, 7×CH_2), 1.60-1.66 (2H, m, CH_2), 2.65 (3H, s, CH_3), 5.31 (1H, s, CH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.5 (CH_3), 14.1 (CH_3), 22.6 (CH_2), 23.0 (CH_2), 29.1 (CH_2), 29.2 (CH_2), 29.3 (CH_2), 31.8 (CH_2), 36.5 (CH_2), 78.1 (CH), 206.7 (C); LRMS (EI) *m/z* 185 (M^+–47, 9%), 155 (25), 141 (34), 113 (100), 85 (66), 57 (46), 56 (20).

4.3. General procedure for the synthesis of *N*-*tert*-butanesulfinyl-α-keto aldimines 3:
To a solution of α-keto aldehyde **2** or hemithioketal **6** (5.0 mmol), and (S_S)-*tert*-butanesulfinamide (**1**, 0.665 g, 5.5 mmol) in dry dichloromethane (15 mL) under argon was added anhydrous copper(II) sulfate (1.760 g, 11.0 mmol) and the reaction mixture was stirred at room temperature for 24 h. The solid was filtered off, washed with ethyl acetate (3×10 mL) and the organic layer was evaporated (15 Torr). The resulting residue was purified by column chromatography (silica gel, hexane/ethyl acetate, 6/1) to yield pure compounds **3**. Yields, physical and spectroscopic data for these compounds follow.

4.3.1. (S_S,*E*)-*N*-(*tert*-Butanesulfinyl)-1-iminopropan-2-one (3a): The representative procedure was followed by using α-keto aldehyde **2a** (0.360 g, 0.344 mL, 5.0 mmol). Purification by column chromatography (hexane/AcOEt, 4:1) yielded **3a** (0.213 g, 4.85 mmol, 97%) as a orange oil; R_f 0.76 (hexane/EtOAc, 2:1); $[\alpha]^{30}_D$ +111.2 (*c* 0.45, CH_2Cl_2); IR (neat) ν 2970, 1705, 1364, 1240, 1090, 1030 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.28 [9H, s, $(CH_3)_3$], 2.50 (3H, s, CH_3), 7.92 (1H, s, CH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.7 (CH_3), 25.4 (CH_3), 58.7 (C), 160.6 (CH), 195.6 (C); LRMS (EI) *m/z* 119 (M^+–56, 100%), 57 (100), 43 (93); HRMS calcd for $C_7H_{13}NO_2S$: 175.0667; found: 175.0664.

4.3.2. (S_S,*E*)-*N*-(*tert*-Butanesulfinyl)-2-imino-1-phenylethan-1-one (3b): The representative procedure was followed by using α-keto aldehyde **2b** (0.67 g, 5.0 mmol). Purification by column chromatography (hexane/AcOEt, 4:1) yielded **3b** (1.10 g, 4.65 mmol, 93%) as a orange oil; R_f 0.65

(hexane/EtOAc, 2:1); $[\alpha]^{30}_D$ +88.2 (*c* 0.65, CH_2Cl_2); IR (neat) ν 2905, 1635, 1580, 1300, 1261, 1167, 1022 839 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.30 [9H, s, $(CH_3)_3$], 7.50-7.66 (3H, m, 3×CH), 8.15 (2H, d, *J* = 7.5 Hz, 2×CH), 8.50 (1H, s, CH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.7 (CH_3), 58.6 (C), 128.7 (CH), 130.1 (CH), 134.3 (C), 134.5 (CH), 161.0 (C), 188.1 (C); LRMS (EI) *m/z* 131 (M^+–106, 80%), 105 (100), 77 (50), 51 (26); HRMS calcd for C_8H_5NO (M^+–$C_4H_{10}SO$): 131.0371; found: 131.0371.

4.3.3. (*S*S,*E*)-1-(4-Bromophenyl)-*N*-(*tert*-butanesulfinyl)-2-iminoethan-1-one (3c): The representative procedure was followed by using hemithioketal **6c** (1.30 g, 5.0 mmol). Purification by column chromatography (hexane/AcOEt, 4:1) yielded **3c** (0.945 g, 3.0 mmol, 60%) as a orange oil; R_f 0.85 (hexane/EtOAc, 2:1); $[\alpha]^{30}_D$ +42.7 (*c* 0.70, CH_2Cl_2); IR (neat) ν 2961, 1662, 1584, 1365, 1280, 1093, 1078 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.29 [9H, s, $(CH_3)_3$], 7.66 (2H, d, *J* = 8.7 Hz, 2×CH), 8.04 (2H, d, *J* = 8.7 Hz, 2×CH); 8.42 (1H, s, CH); ^{13}C NMR (100 MHz, $CDCl_3$) 22.7 (CH_3), 55.8 (C), 129.9 (C), 131.6 (CH), 131.2 (CH), 132.2 (C), 160.6 (CH), 187.0 (C); LRMS (EI) *m/z* 211 (M^+–106, 92%), 209 (90), 185 (100), 183 (92), 157 (35), 155 (40), 75 (36); HRMS calcd for $C_8H_4Br^{79}NO$ (M^+–$C_4H_{10}SO$): 208.9476; found: 208.9473.

4.3.4. (*S*S,*E*)-*N*-(*tert*-Butanesulfinyl)-2-imino-1-(4-methoxyphenyl)ethan-1-one (3d): The representative procedure was followed by using hemithioketal **6d** (1.06 g, 5.0 mmol). Purification by column chromatography (hexane/AcOEt, 4:1) yielded **3d** (0.921g, 3.45 mmol, 69%) as a yellow solid, mp 64-65 ºC (hexane/CH_2Cl_2); R_f 0.60 (hexane/EtOAc, 2:1); $[\alpha]^{30}_D$ +48.7 (*c* 1.00, CH_2Cl_2); IR (neat) ν 2939, 1666, 1590, 1509, 1309, 1261, 1251, 1167, 1022 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.29 [9H, s, $(CH_3)_3$], 3.90 (3H, s, CH_3), 6.99 (2H, d, *J* = 9.0 Hz, 2×CH), 8.16 (2H, d, *J* = 9.0 Hz, 2×CH); 8.48 (1H, s, CH); ^{13}C NMR (100 MHz, $CDCl_3$) 22.7 (CH_3), 55.6 (CH_3), 58.5 (C), 114.1 (CH), 127.6 (C), 131.5 (C), 132.6 (CH), 161.3 (CH), 186.4 (C); LRMS (EI) *m/z* 161 (M^+–106, 60%), 135 (100), 77 (15); HRMS calcd for $C_9H_7NO_2$ (M^+–$C_4H_{10}SO$): 161.0477; found: 161.0478.

4.3.5. (*S*S,*E*)-*N*-(*tert*-Butanesulfinyl)-1-iminoundecan-2-one (3e): The representative procedure was followed by using hemithioketal **6e** (1.16 g, 5.0 mmol). Purification by column chromatography (hexane/AcOEt, 4:1) yielded **3e** (0.79 g, 2.75 mmol, 55%) as a yellow oil; R_f 0.94 (hexane/EtOAc, 2:1); $[\alpha]^{30}_D$ +176.2 (*c* 1.12, CH_2Cl_2); IR (neat) ν 2954, 2923, 2854, 1702, 1458, 1365, 1094 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.88 (3H, t, *J* = 6.3 Hz, CH_2CH_3), 1.24-1.31 [21H, m, 6×CH_2 and $(CH_3)_3$], 1.66 (2H, m, CH_2), 2.86 (2H, t, *J* = 7.5 Hz, CH_2), 7.93 (1H, s, CH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.8 (CH_3), 22.6 (CH_3), 22.8 (CH_2), 23.5 (CH_2), 29.1 (CH_2), 29.2 (CH_2), 29.3 (CH_2), 29.4 (CH_2), 31.8 (CH_2), 38.0 (CH_2), 58.6 (C), 160.5 (CH), 198.2 (C); LRMS (EI) *m/z* 181 (M^+–106, 5%), 152 (19), 124 (56), 98 (90), 55 (100); HRMS calcd for $C_{11}H_{19}NO$ (M^+–$C_4H_{10}SO$): 181.1467; found: 181.1469.

4.4. General procedure for the allylation of *N*-*tert*-butanesulfinyl-α-keto aldimines 3. Synthesis of compounds 10:

To a solution of the corresponding α-keto imine **3** (0.5 mmol) in THF (2 mL) was added the corresponding allylic bromide **4** (0.225 g, 0.161 mL, 1.5 mmol) and indium (0.143 g, 1.25 mmol). The resulting suspension was stirred at 23 ºC for 6 h and after that quenched with brine (4.0 mL) and extracted with ethyl acetate (3×10 mL). The organic layer was dried over anhydrous magnesium sulfate and evaporated (15 Torr). The resulting residue was then purified by column chromatography (silica gel, hexane/ethyl acetate) to yield pure compounds **10**. Yields, physical and spectroscopic data for these compounds follow.

4.4.1. (*S*S,3*R*)-3-Amino-*N*-(*tert*-butanesulfinyl)hex-5-en-2-one (8a): yellow oil; R_F 0.17 (hexane/AcOEt 2:1); $[\alpha]^{30}_D$ +20.3 (*c* 0.65, CH_2Cl_2); IR (neat) ν 2950, 1713, 1639, 1457, 1386, 1364, 1041, 910 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.26 [9H, s, $(CH_3)_3$], 2.25 (3H, s, CH_3), 2.43-

2.65 (2H, m, CH_2), 4.14 (H, q, *J* = 5.0 Hz, CH), 4.56 (H, d, *J* = 5.0 Hz, NH), 5.10-5.16 (2H, m, CH_2), 5.62-5.74 (1H, m, CH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.7 (CH_3), 27.2 (CH_3), 37.2 (CH_2), 56.0 (C), 62.5 (CH), 118.85 (CH_2), 132.1 (CH), 205.9 (C); LRMS (EI) *m/z* 174 (M^+–43, 18%), 161 (28), 146 (13), 118 (100), 91 (24), 57 (37); HRMS calcd for $C_8H_{16}NOS$ (M^+–C_2H_3O): 174.0953; found: 174.0953.

4.4.2. (*S*S)-*N*-(*tert*-Butanesulfinyl)-1-imino-2-methylpent-4-en-2-ol (9a): yellow oil (diastereomeric mixture); R_F 0.45 (hexane/AcOEt 2:1); IR (neat) ν 2970, 1683, 1452, 1312, 1201, 1049, 896 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.21 and 1.22 [9H, 2 s, $(CH_3)_3$], 1.37 and 1.39 (3H, 2 s, CH_3), 2.44-2.48 (2H, m, CH_2), 3.31 (1H, br s, OH), 5.10-5.20 (2H, m, CH_2), 5.51-5.92 (1H, m, CH), 8.06 (1H, s, CH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.1 (CH_3) 21.8 (CH_3), 22.7 (CH_3), 23.1 (CH_3), 44.5 (CH_2), 44.6 (CH_2), 56.8 (C), 74.9 (C), 75.1 (C), 119.7 (CH_2), 131.9 (CH), 172.6 (CH); LRMS (EI) *m/z* 161 (M^+–56, 15%), 146 (60), 120 (100), 91 (13), 57 (50); HRMS calcd for $C_{10}H_{19}NO_2S$: 217.1136; found: 217.1136.

4.4.3. (*S*S,4*S*,5*R*)-5-Amino-*N*-(*tert*-butanesulfinyl)-4-methylocta-1,7-dien-4-ol (10a): The representative procedure was followed by using α-keto imine **3a** (0.0875 g, 0.5 mmol). Purification by column chromatography (hexane/AcOEt, 4:1) yielded **10a** (0.032 g, 0.125 mmol, 25%) as a yellow oil; R_f 0.21 (hexane/EtOAc, 2:1); $[\alpha]^{30}_D$ +18.1 (*c* 1.00, CH_2Cl_2); IR (neat) ν 2892, 1652, 1614, 1475, 1402, 1274, 1167, 1095 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.24 [9H, s, $(CH_3)_3$], 1.26 (3H, s, CH_3), 2.10-2.55 (4H, m, 2×CH_2), 3.21 (1H, dt, *J* = 10.5, 3.0 Hz, CH), 3.82 (1H, d, *J* = 5.1 Hz, NH), 4.01 (1H, br s, OH), 5.02-5.31 (4H, m, 2×CH_2), 5.81-6.10 (2H, m, 2×CH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.9 (CH_3), 26.1 (CH_3), 37.1 (CH_2), 42.1 (CH_2), 56.4 (C), 68.0 (CH), 73.3 (C), 117.1 (CH_2), 117.9 (CH_2), 135.1 (CH), 135.7 (CH); LRMS (EI) *m/z* 203 (M^+–56, 18%), 191 (9), 163 (100), 157 (50), 146 (95), 130 (97), 117 (41), 109 (18), 89 (92), 55 (37); HRMS calcd for $C_9H_{17}NO_2S$ (M^+–C_4H_8): 203.0980; found: 203.0988.

4.4.4. (*S*S,4*S,5*R*)-5-Amino-*N*-(*tert*-butanesulfinyl)-4-phenylocta-1,7-dien-4-ol (10b)**: The representative procedure was followed by using α-keto imine **3b** (0.120 g, 0.5 mmol). Purification by column chromatography (hexane/AcOEt, 4:1) yielded **10b** (0.042 g, 0.13 mmol, 26%) as a yellow oil (58:42 mixture of diastereoisomers); R_f 0.34 (hexane/EtOAc, 2:1); IR (neat) ν 2902, 1475, 1450, 1326, 1274, 1167, 1095 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.18 and 1.21 [9H, 2 s, $(CH_3)_3$], 1.84-1.90 (2H, m, CH_2), 2.41-2.48 (2H, m, CH_2), 2.83 (1H, d, *J* = 6.9 Hz, NH), 3.41-3.46 (1H, m, CH), 3.77 and 4.79 (1H, 2 br s, OH), 4.91-5.30 (4H, m, 2×CH_2), 5.50-5.86 (2H, m, 2×CH), 7.30-7.53 (5H, m, 5×CH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.8 (CH_3), 22.9 (CH_3), 36.0 (CH_2), 37.0 (CH_2), 41.2 (CH_2), 43.4 (CH_2), 56.6 (C), 56.7 (C), 66.3 (CH), 67.1 (CH), 77.0 (C), 77.4 (C), 117.1 (CH_2), 117.2 (CH_2), 118.6 (CH_2), 119.3 (CH_2), 126.7 (CH), 126.8 (CH), 127.2 (CH), 127.3 (CH), 128.1 (CH), 128.2 (CH), 133.5 (CH), 134.3 (CH), 135.4 (CH), 135.7 (CH), 142.2 (C), 142.9 (C); LRMS (EI) *m/z* 265 (M^+–56, 10%), 224 (19), 183 (100), 147 (50), 77 (24), 55 (47); HRMS calcd for $C_{10}H_{20}NOS$ (M^+–C_8H_7O): 202.1266; found: 202.1259.

4.4.5. (*S*S,4*R*,5*S*)-5-Allyl-4-amino-*N*-(*tert*-butanesulfinyl)tetradec-1-en-5-ol (10e): The representative procedure was followed by using α-keto imine **3e** (0,143 g, 0.5 mmol). Purification by column chromatography (hexane/AcOEt, 4:1) yielded **10e** (0.068 g, 0.185 mmol, 37%) as a yellow oil; R_f 0.34 (hexane/EtOAc, 2:1); $[\alpha]^{30}_D$ +56.1 (*c* 1.12, CH_2Cl_2); IR (neat) ν 2920, 2903, 2865, 1665, 1644, 1252, 1235, 1083, 975 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.88 (3H, t, *J* = 5.1 Hz, CH_3), 1.24 [9H, s, $(CH_3)_3$], 1.26-1.34 (16H, m, 8×CH_2), 2.04-2.39 (4H, m, 2×CH_2), 3.29 (1H, td, *J* = 7.8, 1.8 Hz, CH), 3.88 (1H, d, *J* = 1.8 Hz, NH), 5.04-5.15 (4H, m, 2×CH_2), 5.71-5.83 (1H, m, CH), 5.99-6.12 (1H, m, CH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.1 (CH_3), 22.6 (CH_2), 22.7 (CH_2), 22.9 (CH_3), 29.3 (CH_2), 29.5 (CH_2), 29.6 (CH_2), 30.2 (CH_2), 31.9 (CH_2), 37.1 (CH_2), 38.9 (CH_2), 41.8 (CH_2), 56.3 (C), 66.1 (CH), 74.5 (C), 117.0 (CH_2), 117.5 (CH_2), 135.7 (CH), 136.1 (CH);

LRMS (EI) *m/z* 315 (M^+–56, 14%), 274 (35), 233 (28), 141 (60), 113 (100), 85 (60) 71 (55), 57 (47); HRMS calcd for $C_{17}H_{33}NO_2S$ (M^+–C_4H_8): 315.2232; found: 315.2238.

4.5. General procedure for the the RCM of compounds 10. Synthesis of aminocyclohexenols 11:

A mixture of the corresponding 1,7-octadiene **10** (0.25 mmol), ruthenium Hoveyda-Grubbs catalyst (7 mg, 0.0225 mmol) in dry dichloromethane (4.0 mL) was stirred at 40 ºC under argon for 4 h. Then the solvent was evaporated (15 Torr) and the resulting residue was purified by column chromatography (silica gel, hexane/AcOEt) to yield pure compounds **11**. Yields, physical and spectroscopic data for these compounds follow.

4.5.1. (*S*$_S$,1*S*,6*R*)-6-Amino-*N*-(*tert*-butanesulfinyl)-1-methylcyclohex-3-en-1-ol (11a): The representative procedure was followed by using 1,7-octadiene **10a** (0.065 g, 0.25 mmol). Purification by column chromatography (hexane/AcOEt, 4:1) yielded **11a** (0.053 g, 0.23 mmol, 92%), as a brown oil; R_f 0.50 (hexane/EtOAc, 2:1); $[\alpha]^{30}_D$ +58.1 (*c* 1.15, CH_2Cl_2); IR (neat) ν 3002, 2958, 1493, 1470, 1302, 1274, 1115, 1095, 967 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.22 [9H, s, $(CH_3)_3$], 1.26 (3H, s, CH_3), 2.22-2.39 (4H, m, 2×CH_2), 3.31 (1H, m, CH), 3.84 (1H, d, *J* = 5.0 Hz, NH), 5.12 (1H, br s, OH), 5.40-5.70 (2H, m, CH=CH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.6 (CH_3), 25.7 (CH_3), 31.6 (CH_2), 36.8 (CH_2), 55.6 (C), 59.7 (CH), 69.8 (C), 122.7 (CH), 125.5 (CH); LRMS (EI) *m/z* 175 (M^+–56, 28%), 160 (40), 97 (15), 57 (100); HRMS calcd for $C_7H_{13}NO_2S$ (M^+–C_4H_8): 175.0667; found: 175.0664.

4.5.2. (*S*$_S$,1*R*,6*R*)-6-Amino-*N*-(*tert*-butanesulfinyl)-1-phenylcyclohex-3-en-1-ol (11b): The representative procedure was followed by using 1,7-octadiene **10b** as 3:2 diastereomeric mixture (0.080 g, 0.25 mmol). Purification by column chromatography (hexane/AcOEt, 4:1) yielded **11b** (0.026 g, 0.09 mmol, 36%), as a yellow oil; R_f 0.23 (hexane/EtOAc, 2:1); $[\alpha]^{30}_D$ -20.8 (*c* 0.67, CH_2Cl_2); IR (neat) ν 3354, 2979, 1646, 1447, 1364, 1267, 1035 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1,19 [9H, s, $(CH_3)_3$], 1.66-1.73 (1H, m, CH), 2.25-2.40 (1H, m, CH), 2.65-2.78 (1H, m, CH) 2.80-2.94 (1H, m, CH), 3.31 (1H, d, *J* = 10.5 Hz, NH), 3.55-3.61 (1H, m, CH), 5.60-5.73 (1H, m, CH), 5.85-6.00 (1H, m, CH) 7.29-7.40 (3H, m, CH), 7.48-7.55 (2H, m, CH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.7 (CH_3), 32.8 (CH_2), 40.8 (CH_2), 56.0 (C), 62.3 (CH), 73.7 (C), 124.8 (CH), 126.7 (CH), 127.4 (CH), 128.1 (CH), 128.7 (CH), 142.6 (C); LRMS (EI) *m/z* 219 (M^+–74, 10%), 188 (21), 170 (18), 156 (86), 105 (100), 77 (30), 57 (31); HRMS calcd for $C_{16}H_{23}NO_2S$: 293.1449; found: 293.1462.

4.5.3. (*S*$_S$,1*S*,6*R*)-6-Amino-*N*-(*tert*-butanesulfinyl)-1-methylcyclohex-3-en-1-ol (11'b): The representative procedure was followed by using 1,7-octadiene **10b** as 3:2 diastereomeric mixture (0.080 g, 0.25 mmol). Purification by column chromatography (hexane/AcOEt, 4:1) yielded **11'b** (0.021 g, 0.07 mmol, 29%), as a dark brown oil; R_f 0.15 (hexane/EtOAc, 2:1); $[\alpha]^{30}_D$ +47.8 (*c* 1.15, CH_2Cl_2); IR (neat) ν 3338, 2972, 2908, 1679, 1448, 1305, 1126, 1026 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.13 [9H, s, $(CH_3)_3$], 2.24-2.74 (4H, m, CH), 3.53 (1H, br s, OH), 3.65 (1H, d, *J* = 5.7 Hz, NH), 3.77 (1H, q, *J* = 5.7 Hz, CH), 5.69 (1H, m, CH), 5.79 (1H, m, CH), 7.28-7.40 (3H, m, CH), 7.48-7.53 (2H, m, CH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.6 (CH_3), 30.0 (CH_2), 38.2 (CH_2), 56.6 (C), 57.9 (CH), 73.9 (C), 124.0 (CH), 125.4 (CH), 126.1 (CH), 128.1 (CH), 128.5 (CH), 144.3 (C); LRMS (EI) *m/z* 219 (M^+–74, 9%), 188 (7), 170 (18), 157 (13), 156 (100), 155 (12), 105 (40), 77 (15), 57 (13); HRMS calcd for $C_{16}H_{23}NO_2S$: 293.1449; found: 293.1438.

4.6. General procedure for the reduction of *N*-*tert*-butanesulfinyl-α-keto aldimines 3. Synthesis of compounds 12:

To a solution of the corresponding α-keto imine **3** (0.5 mmol) in methanol (3 mL) was added sodium borohydride (57 mg, 1.5 mmol) at 0 ºC. The resulting suspension was stirred at the same temperature for 4 h, and after that quenched with an aqueous saturated solution of ammonium

chloride (10.0 mL) and extracted with ethyl acetate (3×15 mL). The organic layer was dried over anhydrous magnesium sulfate and evaporated (15 Torr). The resulting residue was then purified by column chromatography (silica gel, hexane/ethyl acetate) to yield pure compounds **12**. Yields, physical and spectroscopic data for these compounds follow.

4.6.1. (*S*S)-1-Amino-*N*-(*tert*-butanesulfinyl)propan-2-ol (12a): The representative procedure was followed by using α-keto imine **3a** (0.0875 g, 0.5 mmol). Purification by column chromatography (hexane/AcOEt, 4:1) yielded **12a** (0.075 g, 0.42 mmol, 84%) as a yellow oil (60:40 mixture of diastereoisomers); R_f 0.09 (hexane/EtOAc, 2:1); IR (neat) ν 2958, 1464, 1410, 1356, 1132, 1007; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.14 and 1.20 (3H, 2 d, *J* = 6.3 Hz, CH_3), 1.23 and 1.24 [9H, 2 s, $(CH_3)_3$], 3.01-3.20 and 3.32-3.71 (2H, 2 m, CH_2), 3.83-3.86 and 4.01-4.04 (2H, 2 m, CH, NH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 18.8 (CH_3), 20.3 (CH_3), 22.1 (CH_3), 22.6 (CH_3) 54.2 (CH_2), 55.4 (C), 55.9 (C), 67.7 (CH), 68.0 (CH_2), 68.3 (CH); LRMS (EI) *m/z* 123 (M^+–56, 100), 57 (43); HRMS calcd for $C_3H_9NO_2S$ [M^+–C_4H_8]: 123.0354; found: 123.0346.

4.6.2. (*S*S)-2-Amino-*N*-(*tert*-butanesulfinyl)-1-phenylethan-1-ol (12b): The representative procedure was followed by using α-keto imine **3b** (0.120 g, 0.5 mmol). Purification by column chromatography (hexane/AcOEt, 4:1) yielded **12b** (0.065 g, 0.27 mmol, 54%) as a white solid (59:41 mixture of diastereoisomers), mp 101-102 ºC (hexane/CH_2Cl_2); R_f 0.27 (hexane/EtOAc, 1:1); IR (neat) ν 2957, 2871, 1457, 1416, 1379, 1245, 1099 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.19 and 1.23 [9H, 2 s, $(CH_3)_3$], 3.31-3.36 and 3.84-3.92 (3H, 2 m, CH_2, NH), 4.24 and 4.55 (1H, 2 br s, OH), 4.73-4.77 and 4.90-4.94 (1H, 2 m, CH), 7.20-7.50 (5H, m, CH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.6 (CH_3), 22.7 (CH_3), 54.3 (CH_2), 54.4 (CH_2), 56.0 (C), 56.1 (C), 73.0 (CH), 73.9 (CH), 130.0 (CH), 126.1 (CH), 127.6 (CH), 127.8 (CH), 128.4 (CH), 128.5 (CH), 141.4 (C), 141.5 (C); LRMS (EI) *m/z* 185 (M^+–56, 20%), 146 (35), 121 (68), 91 (85), 79 (100), 57 (74); HRMS calcd for $C_8H_{11}NO_2S$ (M^+–C_4H_8): 185.0510; found: 185.0494.

4.6.3. (*S*S)-2-Amino-1-(4-bromophenyl)-*N*-(*tert*-butanesulfinyl)ethan-1-ol (12c): The representative procedure was followed by using α-keto imine **3c** (0.158 g, 0.5 mmol). Purification by column chromatography (hexane/AcOEt, 4:1) yielded **12c** (0.124 g, 0.39 mmol, 78%) as a white solid (56:44 mixture of diastereoisomers), mp 80-82 ºC (hexane/CH_2Cl_2); R_f 0.08 (hexane/EtOAc, 2:1); IR (neat) ν 2952, 1450, 1422, 1325, 1245, 1113, 958, 658 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.20 and 1.24 [9H, 2 s, $(CH_3)_3$], 3.21-3.40 (2H, m, CH_2), 3.61-3.92 (1H, m, NH), 4.72 and 4.91 (1H, 2 dd, *J* = 8,7, 3.3 Hz, CH), 7.20-7.30 (2H, m, 2×CH), 7.47 (2H, d, *J* = 8.3 Hz, 2×CH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.6 (CH_3), 22.7 (CH_3), 54.4 (CH_2), 54.5 (CH_2), 56.1 (C), 56.2 (C), 72.4 (CH), 73.4 (CH), 121.4 (C), 121.6 (C), 127.7 (CH), 127.8 (CH), 131.5 (CH), 131.6 (CH), 140.2 (C), 140.5 (C); LRMS (EI) *m/z* 264 (M^+–56, 15%), 262 (17%), 196 (38), 184 (92), 183 (30), 182 (100), 181 (33), 156 (41), 154 (45); HRMS calcd for $C_8H_{10}Br^{79}NOS$ (M^+–C_4H_8): 262.9616; found: 262.9627.

4.6.4. (*S*S)-2-Amino-*N*-(*tert*-butanesulfinyl)-1-(4-methoxyphenyl)ethan-1-ol (12d): The representative procedure was followed by using α-keto imine **3d** (0.135 g, 0.5 mmol). Purification by column chromatography (hexane/AcOEt, 4:1) yielded **12d** (0.120 g, 0.45 mmol, 89%) as a white solid (57:43 mixture of diastereoisomers), mp 76-77 ºC (hexane/CH_2Cl_2); R_f 0.05 (hexane/EtOAc, 2:1); IR (neat) ν 2950, 1470, 1459, 1358, 1330, 1200, 1135, 1032 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.20 and 1.24 [9H, s, $(CH_3)_3$], 3.31-3.42 (2H, m, CH_2), 3.80 (3H, s, CH_3), 4.1 (1H, br s, OH), 4.70-4.74 and 4.87-4.90 (1H, 2 m, CH), 6.88 (2H, dd, *J* = 8.7, 1.5 Hz, 2×CH), 7.23-7.31 (2H, m, CH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.6 (CH_3), 22.7 (CH_3), 54.3 (CH_2), 54.4 (CH_2), 55.3 (CH_3), 55.9 (C), 56.0 (C), 72.6 (CH), 73.6 (CH), 113.9 (CH), 127.2 (CH) 127.3 (CH) 133.4 (C) 133.5 (C), 159.1 (C), 159.3 (C); LRMS (EI) *m/z* 165 (M^+–106, 20%), 137 (86), 135 (100), 119 (90), 109 (80), 81 (84); HRMS calcd for $C_9H_{11}NO_2$ (M^+–$C_4H_{10}SO$): 165.0790; found: 165.0782.

4.6.5. (S_S)-1-Amino-*N*-(*tert*-butanesulfinyl)dodecan-2-ol (12e): The representative procedure was followed by using α-keto imine **3e** (0,143 g, 0.5 mmol). Purification by column chromatography (hexane/AcOEt, 4:1) yielded **12e** (0.081 g, 0.28 mmol, 56%) as a yellow oil (54:46 mixture of diastereoisomers); R_f 0.13 (hexane/EtOAc, 2:1); IR (neat) ν 2954, 2923, 2854, 1455, 1408, 1375, 1271, 1137, 1094, 985 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.88 (3H, t, J = 6.6 Hz, CH_3), 1.23 and 1.24 [9H, 2 s, $(CH_3)_3$], 1.24-1.32 (14H, m, 7×CH_2), 1.38-1.43 (2H, m, CH_2), 2.91-3.10 and 3.15-3.33 (2H, 2 m, CH_2), 3.58-3.66, 3.71-3.79, 3.80-3.92 (2H, 3 m, NH, CH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.1 (CH_3), 22.6 (CH_3), 22.7 (CH_3), 25.6 (CH_2), 29.3 (CH_2), 29.5 (CH_2), 29.6 (CH_2), 31.9 (CH_2) 34.4 (CH_2), 34.6 (CH_2), 52.5 (CH_2), 52.9 (CH_2), 55.8 (C). 56.1 (C), 70.8 (CH), 71.6 (CH); LRMS (EI) *m/z* 235 (M^+–56, 16%), 155 (45), 141 (55), 113 (100), 85 (76), 71 (48), 57 (35), 56 (24); HRMS calcd for $C_{15}H_{33}NO_2S$: 291.2232; found: 291.2235.

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GRAPHICAL ABSTRACT

Stereoselective Allylation and Reduction of *N*-*tert*-Butane-sulfinyl-α-keto Aldimines

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